

# Structure and phase diagram of the $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6$ system

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A complex study was carried out on  $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6$  binary system by means of differential thermal analyses (DTA), X-ray diffraction as well as infrared (IR), and Raman spectroscopy. Although the system exhibits a simple eutectic at 83 wt %  $\text{Na}_2\text{B}_4\text{O}_7$  and  $T_e = 642^\circ\text{C}$ , interesting structural changes of borate glasses formed have been evidenced by means of IR and Raman spectroscopy. Over 80–100 wt %  $\text{Na}_2\text{B}_4\text{O}_7$  range  $\text{AlF}_6^{3-}$  anions are diluted in the vitreous matrix without significant structural changes while the further increase of  $\text{Na}_3\text{AlF}_6$  content diminishes the concentration of  $\text{BO}_4$  groups and promotes the appearance of complex anions  $\text{AlF}_x^{(x-3)-}$  ( $x = 6, 5, 4$ ) as well as the possible new  $\text{BF}_4^-$  and/or  $\text{BO}_3\text{F}_4^-$  species. © 1999 Kluwer Academic Publishers

## 1. Introduction

As part of a general study regarding the phase diagram and the structure of  $\text{NaCl-Na}_3\text{AlF}_6\text{-Na}_2\text{B}_4\text{O}_7\text{-TiO}_2$  quaternary system, this contribution presents the results obtained in a first stage with  $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6$  binary subsystem. The interest focused by this investigation is related to the suitability of  $\text{NaCl-Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6\text{-TiO}_2$  molten electrolyte in obtaining high purity  $\text{TiB}_2$  powders by electrosynthesis [1, 2]. These powders are regarded as a promising precursor in the obtaining of some ceramics with exceptional electrical, thermochemical and chemical properties, which are very attractive as building materials in various advanced technologies. The cathodic electroreduction process of titanium and boron ions as well as of  $\text{TiB}_2$  formation is practically unknown because of the absence of information regarding the structural entities existing in the molten electrolyte. The only data available in literature refer to the phase diagram of the following binary subsystems:  $\text{Na}_3\text{AlF}_6\text{-NaCl}$  [3],  $\text{Na}_2\text{B}_4\text{O}_7\text{-NaCl}$  [4],  $\text{Na}_3\text{AlF}_6\text{-TiO}_2$  [5], which offer no necessary information in the sense already mentioned.

Approaching the binary  $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6$  system, the authors aimed at clearing up the specific interaction between the  $\text{Na}_3\text{AlF}_6$ , solvent melt, and  $\text{Na}_2\text{B}_4\text{O}_7$ , which is one of the electroactive component of the electrolyte. As well known, the borate melts exhibit the so called "boron anomaly" associated with the modification of its coordination number. Therefore it was necessary to clarify the influence exerted by  $\text{Na}_3\text{AlF}_6$  addition on the structural entities as function of modifier concentration [6–11]. On the other hand to show up the vitreous state in this system requires the estab-

lishing of the concentration range over which the melt retains an adequate fluidity which is favorable to the unfolding of electrolysis in normal conditions.

The study was carried out by DTA measurements, X-ray diffraction, IR and Raman spectroscopy, over the whole concentration range of the two components. In the following are discussed the results thus obtained.

## 2. Experimental

The chemicals employed were p.a. grade reagents:  $\text{Na}_3\text{AlF}_6$  (Riedel de Haen) and  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (Reactivul). The anhydrous borate was obtained by dehydration (slow increase of temperature up to  $320^\circ\text{C}$ ), followed by the melting of salt up to  $900^\circ\text{C}$ , for 10 min. The mixtures studied were obtained by weighing adequate quantities of the two components as fine powders, followed by mechanical homogenization. Afterwards all mixtures were dried at  $100^\circ\text{C}$  for 24 h and stored in a desiccator on  $\text{P}_2\text{O}_5$ . The vitreous melts were recrystallized by means of a supplementary thermal treatment, at  $560^\circ\text{C}$  for 23 h in a programmed furnace Vulcan TM 3-130.

The pellets employed in determining IR were obtained by mixing 1 mg of sample powder (previously premelted in a platinum crucible 30 min then cooled in atmosphere) with 200 mg CsI. The samples used in recording Raman spectra were weighted into a nitrogen atmosphere glove box with a water content less than 1 ppm. In order to homogenise the mixtures they were premelted 15 min at  $750\text{--}1000^\circ\text{C}$  in a glassy carbon crucible under argon atmosphere. All the samples were cooled slowly at room temperature. Especially for

the glassy samples, the melting process was repeated more than two times in order to remove the bubbles. All pellets obtained (0.15–0.25 g each) were stored into the glove box. Owing to the high corrosivity of fluorides, the graphite windowless cell technique was used in order to obtain Raman spectra of melts. The graphite cell containing the sample was introduced into an optical quartz tube under argon atmosphere.

The thermal behaviour of samples studied over 20–1050 °C interval was analyzed with a CD 103 derivatograph MOM-Budapest at a heating rate of 5°/min using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference.

The diffraction measurements were performed on a HZG4A diffractometer with a Ni filter, having a  $2\theta$  type reflection geometry and using CuK $\alpha$  radiation. The X-ray diffractograms were recorded both on rapidly quenched specimens and on crystallized powders.

Additional information on the structure resulted from IR spectra obtained by means of a IR Carl Zeiss Jena type M80 spectrometer. The recording of spectra were effected within 4000–200 cm<sup>-1</sup>.

The vitreous transition point,  $T_g$ , was also determined with a DSC du Pont 1090 apparatus at a rate of 10 °C/min.

The 514.5 and 488 nm lines of an Ar<sup>+</sup> laser (Spectra Physics model 164-08) were used to excite the Raman spectra. The power was adjusted to be 200–350 mW just before entering the optical cell. The scattered light was collected at an angle of 90° and analysed with a Spex 1403, 0.85-m double monochromator equipped with a –20 °C cooler RCA photomultiplier and EG & G/ORTEC photon counting and chopper lock-in amplifier electronics. The furnace used for recording high-temperature Raman spectra was described in detail elsewhere [12] having a maximum operating temperature of 900 °C. The Raman spectra of melts with Na<sub>3</sub>AlF<sub>6</sub> rich content were measured using another experimental Raman set-up T-6400 (Jobin Yvon), equipped with Spectraview-20 2D<sup>TM</sup> liquid N<sub>2</sub>-cooled CCD detector in a triple configuration and a furnace having a 20–1000 °C temperature range of operation. The experimental systems used in this work were interfaced with a personal computer and the spectra were saved in digital form. Also two different polarizations were used for recording the spectra namely VV and HV.

### 3. Results and discussion

#### 3.1. The phase diagram

The DTA data obtained for the two single components of the system, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and Na<sub>3</sub>AlF<sub>6</sub>, and for nine mixtures, chosen from all 13 mixtures investigated, covering the whole concentration range, are shown in Fig. 1. One can note on the specific curve of Na<sub>3</sub>AlF<sub>6</sub> an endothermal polymorphous transformation at about 567 °C, which originates in the transition from monoclinic crystallization system ( $\alpha$  Na<sub>3</sub>AlF<sub>6</sub> form) to the cubic one [12]. Regarding the behaviour of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> one should note the strong exothermal effect on crystallization which occurs at concentrations higher than 50 wt % Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> that subsequently cancels the effect of polymorphous transformation discussed above.

The liquidus curve of this system is shown in Fig. 2 and evidences the presence of a simple eutectic point at  $T_e = 642$  °C and 83% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. It is worth mentioning that the DTA recordings carried out at various rates of heating, 2.5, 5 and 7.5°/min, indicated a standard deviation of 0.94 for the melting temperature determined. The presence of transparent colorless glasses were observed over 80–100 wt % Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> concentration range.

#### 3.2. X-ray diffraction spectra

It was noted that the diffractogram of cryolite thermally treated at 560 °C and untreated are identical and evidence no polymorphous transformations from the monoclinic to cubic system, while the diffractogram of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> exhibits the usual development of the glassy state. Regarding the spectra obtained in crystallized binary mixtures, as evidenced in Fig. 3, there is no indication on the presence of any new compound.

#### 3.3. IR spectra

According to the data in literature the mid-IR spectroscopy, over 400–1700 cm<sup>-1</sup> is a sensitive method of determining the network of borate glass [12–14] as well as the state of AlF<sub>x</sub><sup>(x-3)-</sup> ion [15]. It is worth mentioning the fact that up to 10 wt % Na<sub>3</sub>AlF<sub>6</sub> content the glassy structure of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> is not considerably altered, except for the slight shift of the widened shoulder at 540 cm<sup>-1</sup> compared to 530 cm<sup>-1</sup> specific to the pure random glass (see Fig. 4a). This behaviour suggests that over this concentration domain, AlF<sub>6</sub><sup>3-</sup> anions are diluted in the vitreous matrix of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> [14]. According to Fig. 4, the further increase of Na<sub>3</sub>AlF<sub>6</sub> content produces interesting changes of the three characteristic regions of borate glass as:

(i) *BO<sub>3</sub> stretching*. In the range 1200–1550 cm<sup>-1</sup>, at high cryolite concentrations, a new band at 1250 cm<sup>-1</sup> arises which is not characteristic to the diborate groups of pure Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> glasses [16] and suggests the formation of boroxol rings and probably, of tri-, tetra- and pentaborate groups (see Fig. 4b).

(ii) *BO<sub>4</sub> stretching*. The decrease of the intensity of bands over 800–1200 cm<sup>-1</sup> range as the content of Na<sub>3</sub>AlF<sub>6</sub> increases suggests the diminishing of BO<sub>4</sub> groups concentration. Given the fact that the formation of glassy phase in borate systems is directly related to the presence of boron atoms in fourfold coordination [16] it becomes obvious that Na<sub>3</sub>AlF<sub>6</sub> plays the role of a glass network modifier. With the increase of cryolite content, as one can see in Fig. 4, the splitting of 800–1200 cm<sup>-1</sup> bands takes place, the peaks at 1020 and 880 cm<sup>-1</sup> being specific to the crystalline compounds of tetraborate [17]. A similar splitting of the bands specific to the stretching of B–O bonds in BO<sub>4</sub> tetrahedron is illustrated in Fig. 5 for single Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> vitreous and crystallized at 560 °C. Thus, the diminishing of the intensities of bands in Fig. 4 suggests a systematic decrease of the tetracoordinated boron atom groups and partial destruction of the vitreous network

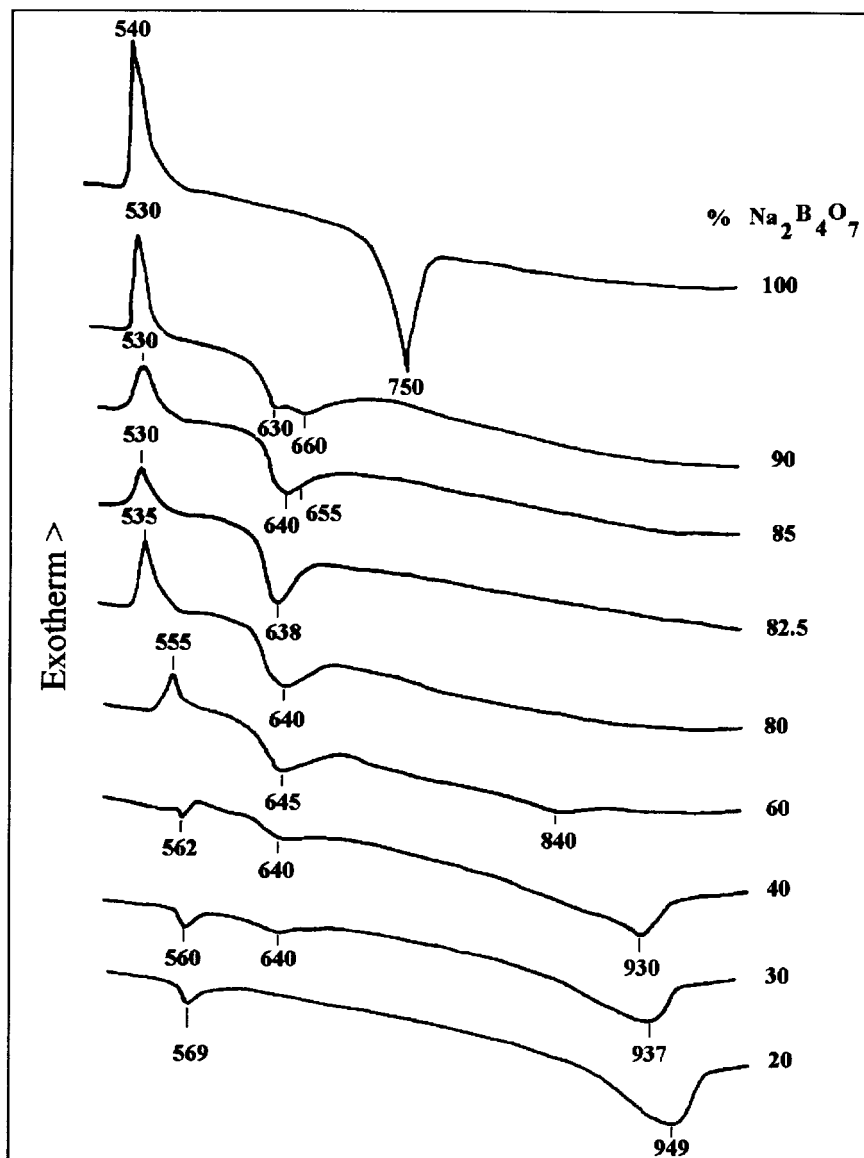


Figure 1 DTA curves for  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_3\text{AlF}_6$  binary system of various composition (wt% content).

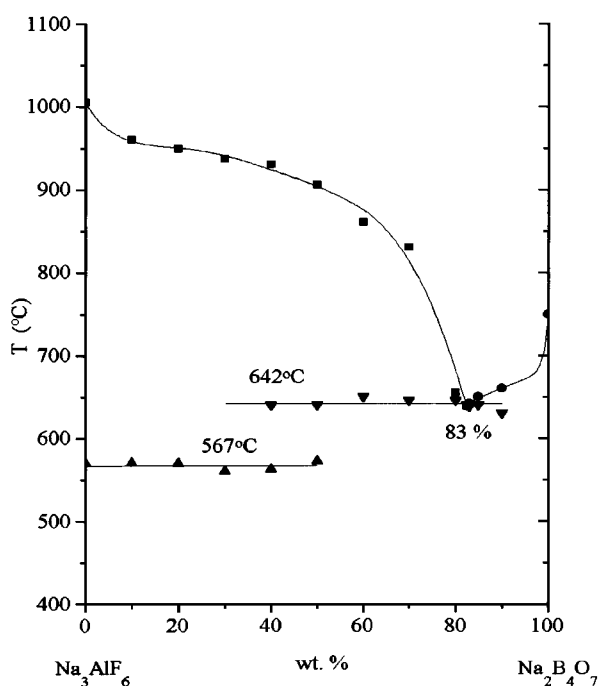


Figure 2 Phase diagram of  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_3\text{AlF}_6$  system.

by crystallization induced with increasing of  $\text{Na}_3\text{AlF}_6$  concentration.

(iii) *B-O-B bending*. According to Fig. 4, in case of wave numbers below  $800\text{ cm}^{-1}$ , besides the bands characteristic for cryolite, the band at  $720\text{ cm}^{-1}$  is also recorded which is specific to bending vibrations of oxygen bridges between two trigonal boron atoms, B [10, 11, 17].

The discussion above shows, beyond doubt, that in the glasses formed with  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_3\text{AlF}_6$  binary system the  $\text{BO}_4$  units specific for vitreous state are partially destroyed in favor of tri-, tetra- and pentaborate groups ( $1070\text{ cm}^{-1}$ ), and of boroxol rings, tri-, tetra- and pentaborate groups ( $1250\text{ cm}^{-1}$ ) as the increasing  $\text{Na}_3\text{AlF}_6$  content favors the crystallization process of glasses.

However, the vitreous state of the eutectic mixture is a stable one. Thus, it was established that the glass transition in the mixture with 82.5 wt%  $\text{Na}_2\text{B}_4\text{O}_7$  (the closest investigated composition of the eutectic one, in Fig. 2) corresponds to  $T_g = 345\text{ }^\circ\text{C}$  (determined by DSC measurements) compared to the melting temperature of

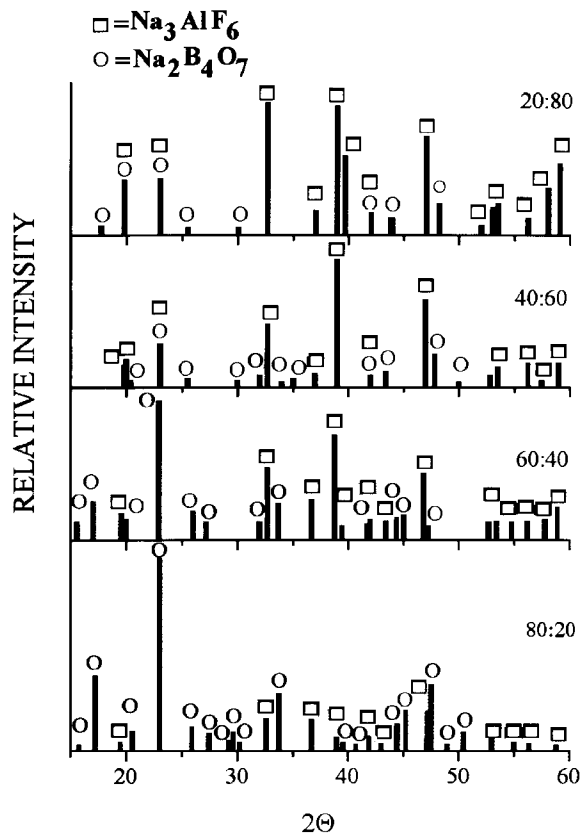


Figure 3 X-ray diffractograms for  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_3\text{AlF}_6$  system at various compositions (wt % content).

the mixture  $T_m = 638^\circ\text{C}$ . The value obtained with Hoch relation [18, 19] equals  $T_g = 331.9^\circ\text{C}$ , and is in satisfactory agreement with the experimental one. Considering the large difference  $T_m - T_g$  it is obvious [20] that the eutectic mixture is a stable glass which is very likely to be retained as  $\text{Na}_2\text{B}_4\text{O}_7$  when the concentration is increased.

It is also worth mentioning that the addition of fluorine anion, owing to its similarity with oxygen anion regarding electronegativity and ionic radius, can cause, in a borate system, the conversion of the  $\text{BO}_3$  groups into  $\text{BO}_3\text{F}$  and, more unlikely, to  $\text{BO}_2\text{F}_2$  [21]. However, the strong broad band that is centered around  $1000\text{ cm}^{-1}$  can correspond not only to the  $\text{BO}_3\text{F}$  units but also to diborate groups, which make very difficult the assignment. Recent data [22] suggest that diborate groups, which make up the majority of structural entities in the  $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$  glass, contain  $\text{F}^-$  anions attached to four-fold boron atoms.

### 3.4. Raman spectra

The spectra of the glasses in the  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_3\text{AlF}_6$  system, with VV polarisation are illustrated in Fig. 6. Because the specific bands of these spectra are in very close agreement with those by Kamitsos [16], in the  $\text{MgO}\text{-Na}_2\text{O}\text{-B}_2\text{O}_3$  system, and by Dwivedi [23], in the  $x\text{R}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$  system (where  $\text{R} = \text{Li}, \text{Na}, \text{K}$ ), their assignment was similar.

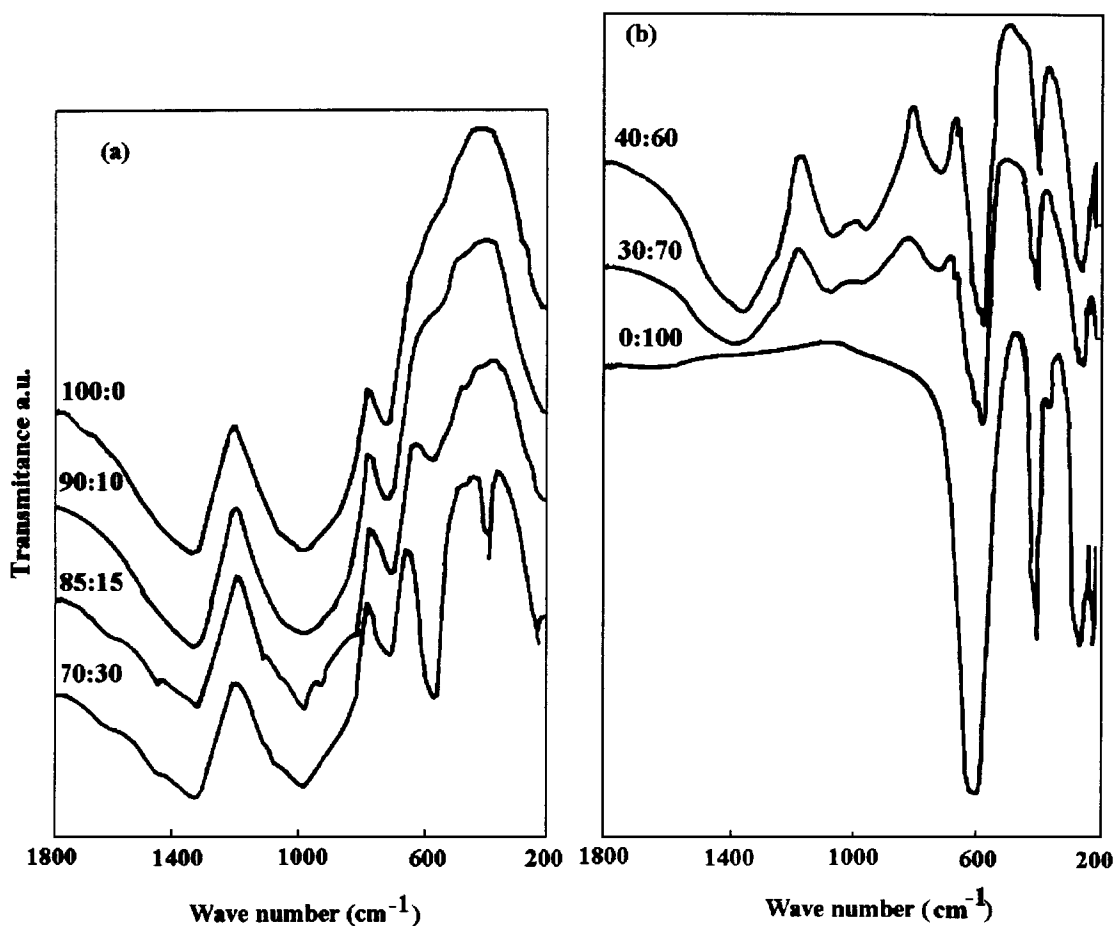


Figure 4 IR spectra of  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{Na}_3\text{AlF}_6$  binary system: (a) 100–70 wt %  $\text{Na}_2\text{B}_4\text{O}_7$  and (b) 60–100 wt %  $\text{Na}_3\text{AlF}_6$ .

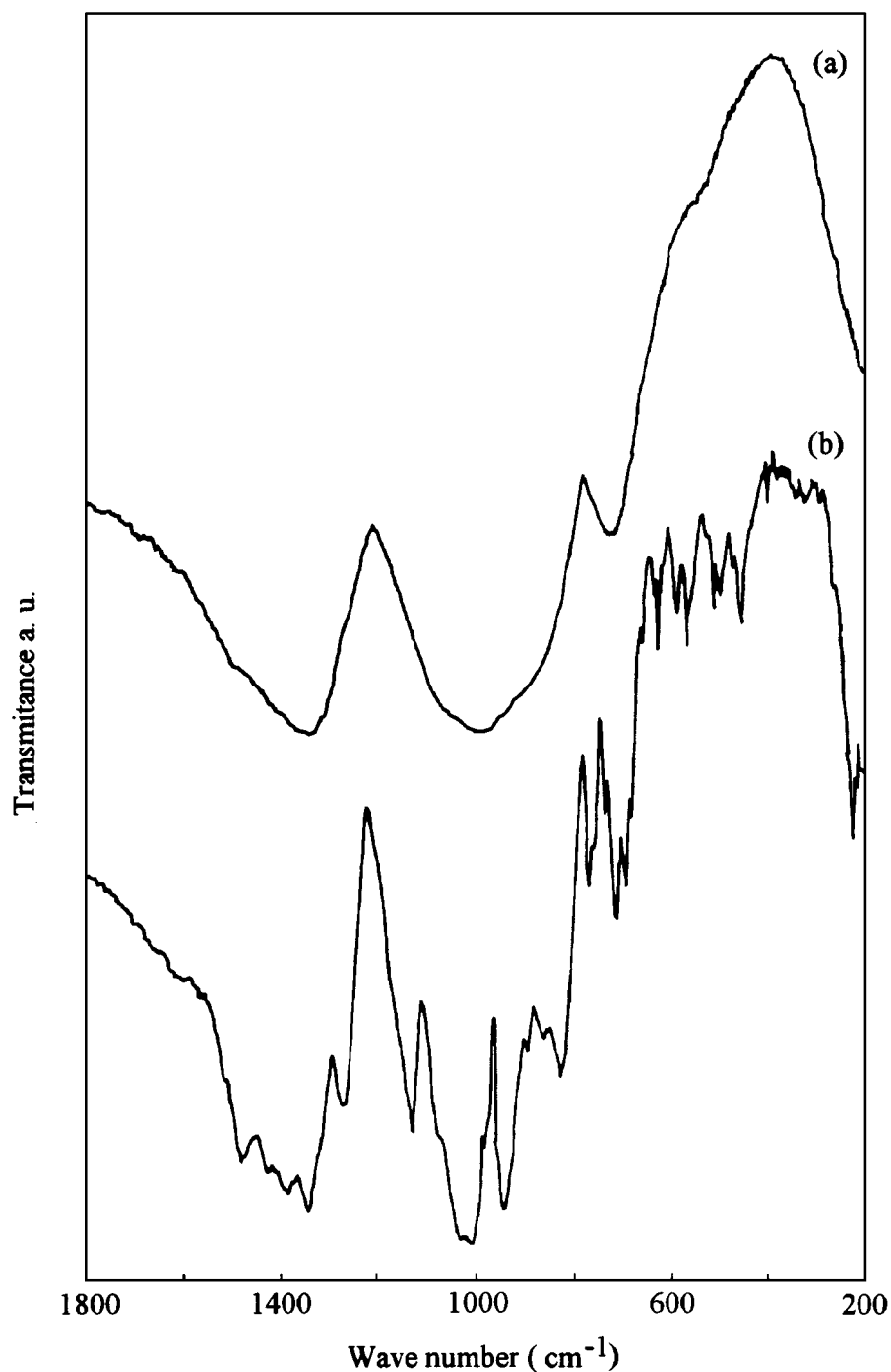


Figure 5 Comparative study of the IR spectra obtained on  $\text{Na}_2\text{B}_4\text{O}_7$  pellets: (a) vitreous state and (b) crystallized glasses.

Thus, the low frequency Raman spectra, LFRS, are dominated by the “boson” peak [23]. According to the expectations [24], the boson peak shifts towards higher frequency, from 62 to 69  $\text{cm}^{-1}$ , when the concentration of  $\text{Na}_2\text{B}_4\text{O}_7$  increases. On the contrary, in the presence of  $\text{Na}_3\text{AlF}_6$  a weakening of  $\text{Na}_2\text{B}_4\text{O}_7$  network-structure takes place which makes the glass more fragile.

In the high frequency region of the Raman spectrum of pure  $\text{Na}_2\text{B}_4\text{O}_7$ , the first band is observed at 500  $\text{cm}^{-1}$  and its shoulder at about 454  $\text{cm}^{-1}$ . The bands in this region were tentatively assigned to “isolated” diborate units. According to Dwiwedi [23] the sharpest band at 766  $\text{cm}^{-1}$  possibly belongs to a six-membered ring involving two  $\text{BO}_4$  groups, consequently the absence of any band at about 800  $\text{cm}^{-1}$ , in Fig. 6, invalidates

the presence of boroxol rings indicated by IR spectra in Fig. 4.

Regarding the band at 860  $\text{cm}^{-1}$  it is attributed to the symmetric stretching vibration of B–O–B bonds from pyroborate units ( $\text{B}_2\text{O}_5^{4-}$ ), while the pentaborate and tetraborate units are responsible for the band at about 964  $\text{cm}^{-1}$ . This latest band shows a shoulder at 912  $\text{cm}^{-1}$  without assignment for pure  $\text{Na}_2\text{B}_4\text{O}_7$  glass. The diborate units are represented by the 1126  $\text{cm}^{-1}$  band. The B–O<sup>-</sup> bonds attached to large borate groups are responsible for the band at 1430–1500  $\text{cm}^{-1}$ , but in this region there is also a shoulder at about 1370  $\text{cm}^{-1}$  that could be related to non-ring  $\text{BO}_3$  groups [25].

In the Table I are summarized the Raman bands of pure  $\text{Na}_2\text{B}_4\text{O}_7$  as measured by Chryssikos [16],

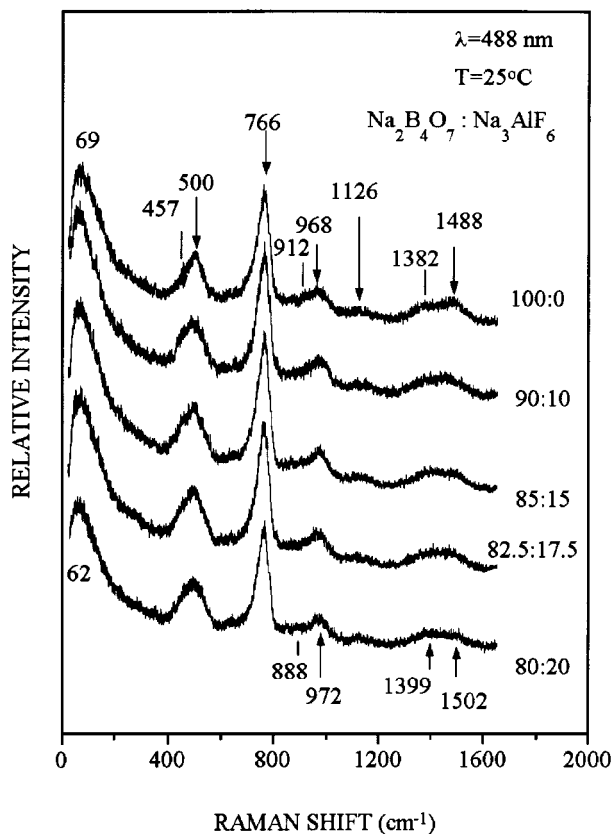


Figure 6 Raman spectra of  $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6$  glasses.

Dwivedi [23] and recorded in the present work (33%  $\text{Na}_2\text{O}$  : 67%  $\text{B}_2\text{O}_3 = \text{Na}_2\text{B}_4\text{O}_7$ , molar%). Therefore the spectrum of  $\text{Na}_2\text{B}_4\text{O}_7$  presented in this contribution is quite close to that one recorded by Dwivedi [23].

The addition of  $\text{Na}_3\text{AlF}_6$  ( $3\text{NaF}\cdot\text{AlF}_3$ ) to  $\text{Na}_2\text{B}_4\text{O}_7$  does not change significantly the borate glass structure, confirming the behaviour reported for IR spectra. However, with the increasing content of cryolite in the glasses, a small blue frequency shift is observed mainly for the bands located in the region  $850\text{--}1000\text{ cm}^{-1}$ . NaF addition would weaken the network structure more efficiently than  $\text{Na}_2\text{O}$  in  $\text{B}_2\text{O}_3$ , which could be due to the presence of  $\text{BO}_3\text{F}$  instead of  $\text{BO}_4$  [26]. In fact, Fukunaga has noticed that the glass transition temperature,  $T_g$ , decreases as NaF concentration increases.

TABLE I Peak positions ( $\text{cm}^{-1}$ ) for  $x\text{Na}_2\text{O}:(100-x)\text{B}_2\text{O}_3$  glasses (% molar)

Present work	Dwivedi [23]		Chryssikos [16]	
	30%	35%	33%	53%
69	51	56		
457				
500	507	520	490	507
—	663	630	675	635
766	763	762	772	760
860	854	855		
912	888	885		
968	952	954	945	960
1126	1120	1121	1120	1120
1382				
1488	1430	1436	1430	1490

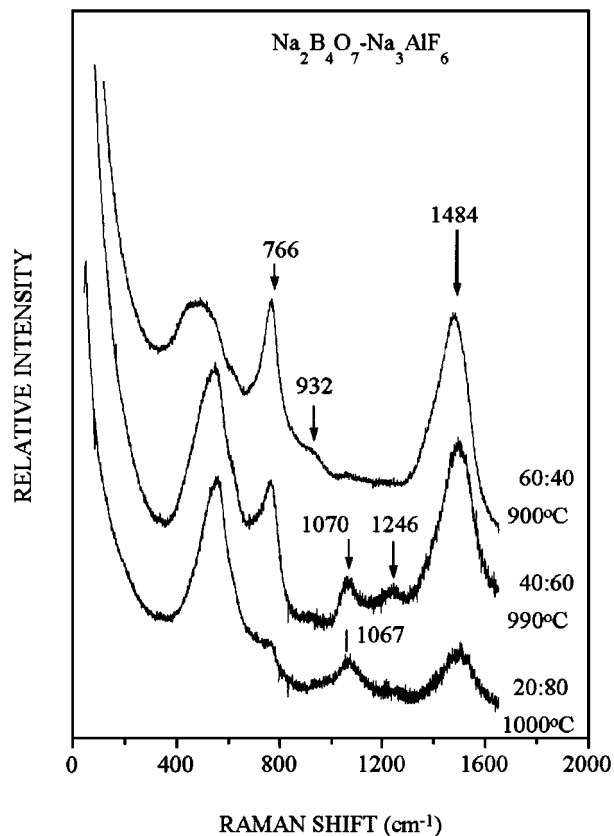


Figure 7 Raman spectra of the  $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6$  melts at various temperatures and compositions (wt % content).

Because the melts which are important in the electrosynthesis of  $\text{TiB}_2$  should occupy a position outside rich concentration range of the  $\text{Na}_2\text{B}_4\text{O}_7$ , where stable glasses are formed, the Raman spectra were recorded and deconvoluted in Figs 7 and 8, for the following compositions: 20, 40 and 60 wt %  $\text{Na}_2\text{B}_4\text{O}_7$ . Their evolution suggests the following phenomena:

(i) the decreasing intensity of the peak at about  $763\text{ cm}^{-1}$  and its increasing at about  $433\text{ cm}^{-1}$  that could result from the break up of six membered borate ring into  $\text{B}\Theta_3$  units ( $\Theta = \text{non-bridging oxygen}$ ), previously suggested by Fukunaga [27],

(ii) the vanishing at elevated temperature of the  $1120\text{ cm}^{-1}$  band that is assigned to the diborate units proves that the presence of the high-membered rings in the glassy network is favored to a lesser extent when temperature increases,

(iii) the coexistence in equilibrium of various species [28]:  $\text{AlF}_6^{3-}$  ( $\nu = 515\text{ cm}^{-1}$ ),  $\text{AlF}_5^{2-}$  ( $\nu = 555\text{ cm}^{-1}$ ) and  $\text{AlF}_4^-$  ( $\nu = 622\text{ cm}^{-1}$ ) in the cryolite-rich melt.

Analogous to Quist assignment of the  $1070\text{ cm}^{-1}$  band [28], the band at about  $1067\text{ cm}^{-1}$  may be assigned to  $\text{BF}_4^-$  species formed by substitution of the oxygen anions with  $\text{F}^-$  anions resulting from cryolite dissociation. The band at about  $770\text{ cm}^{-1}$  can belong not only to six-membered borate rings with a  $\text{BO}_4$  but to  $\text{BO}_3\text{F}$  [21] and  $\text{BF}_4$  [29] as well, which make their assignment very difficult.

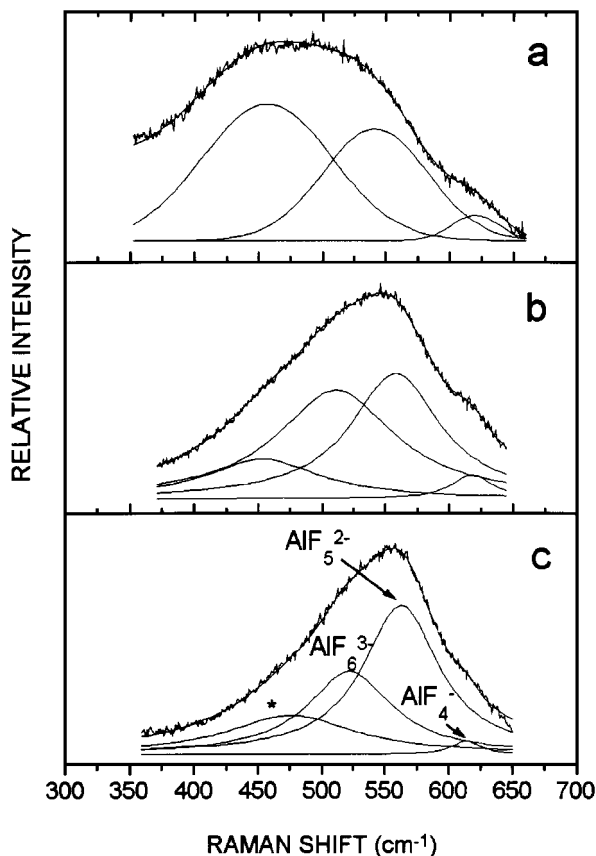


Figure 8 Deconvoluted Raman spectra of  $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6$  melts: (a) 60 wt %  $\text{Na}_2\text{B}_4\text{O}_7$ , (b) 40 wt %  $\text{Na}_2\text{B}_4\text{O}_7$  and (c) 20 wt %  $\text{Na}_2\text{B}_4\text{O}_7$ .

#### 4. Conclusions

One can conclude that although DTA data obtained in the  $\text{Na}_2\text{B}_4\text{O}_7\text{-Na}_3\text{AlF}_6$  binary mixtures evidences the presence of a simple eutectic; structural studies supplied by X-ray diffraction, IR and Raman spectroscopy offer more detailed information on the structural entities and on the modifications of the borate melts occurring at variable  $\text{Na}_3\text{AlF}_6$  content. Thus, it was proved that cryolite plays the role of modifier promoting the so called phenomenon of boron anomaly, concerning the changing of the coordination of  $\text{O}^{2-}$  and/or  $\text{F}^-$  anions around the central boron atom. The presence of oxyfluoroborate groups in this system is still a matter of controversy.

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